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Effect of Plasticization on the Performance of a Photorefractive Polymer

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A systematic study of the effect of plasticization on the photorefractive performance of a poly(*N*-vinylcarbazole) (PVK) based polymer composite is presented. It is shown that *N*-ethylcarbazole (ECZ) can be used as an efficient plasticizer, leading to a large increase of the gain coefficient and the diffraction efficiency, which arises solely due to an improvement in the orientational mobility of the dispersed nonlinear optical molecules. Phase separation, which is observed at samples with a high ECZ concentration, sets the upper limit. The steady state and the kinetics of the photorefractive gratings in the plasticized samples are discussed. The measurements suggest a high value of the saturation field and a response time that is limited by photogeneration. A configuration is described, where prisms are employed to couple light into and from the sample, resulting into a higher two-beam coupling gain and diffraction efficiency.

1. Introduction

Photorefractive materials have been investigated thoroughly over the last 30 years due to their potential application in image processing and three-dimensional optical data storage devices. Under nonuniform illumination of a photorefractive material, photoexcited charges migrate out of the illuminated areas and eventually get trapped in the dark areas, giving rise to a spatially varying electric field (space charge field). This space charge field alters the index of refraction due to the linear electrooptic (Pockels) effect. In this way, a refractive index grating that is a replica of the illumination pattern is produced.[1] Although, such a replication can also be achieved with other mechanisms, such as photochemistry and thermorefraction,[2] the photorefractive effect possesses a combination of characteristics that make it unique: Very high nonlinearities can be achieved with even weak laser beams, as a result of the integrating nature of the effect. The resulting refractive index gratings are reversible, as uniform illumination erases the space charge field. Another very important characteristic is the existence of spatial phase shift between the illumination pattern and the refractive index grating, which gives rise to steady state asymmetric energy exchange between two laser beams.[1]

Potential photorefractive materials must possess the following properties: charge generation, transport and trapping, and an electrooptic response. Until recently, the main materials of interest were inorganic electrooptic crystals such as lithium niobate or barium titanate. The observation of photorefractivity in a polymer[3] has led to the development of a large variety of photorefractive polymer structures (see review papers refs 4, 5).

Most of the photorefractive polymers reported so far are host−guest composites, consisting of a charge-transporting matrix (usually poly(*N*-vinylcarbazole), PVK) doped with a high concentration of nonlinear optical (NLO) molecules to introduce the necessary electrooptic response. To break the centrosymmetry of the material and to obtain a macroscopic electrooptic response, these molecules are oriented by electric field poling.[6] The efficiency of the poling process is strongly dependent on the orientational freedom of the NLO molecules: At temperatures well below the glass transition temperature (T_g), the polymer chains are frozen and the orientational mobility of the NLO molecules is very low. As the temperature is raised close to the T_g, the orientational freedom of the NLO molecules increases, allowing an efficient poling.

When large amounts of NLO molecules are incorporated, the T_g of PVK (200 °C) is substantially lowered, which is desirable, since then the NLO molecules can be oriented even at room temperature.[7] Recently however, a large increase in the photorefractive performance of a PVK-based polymer was observed after the incorporation of additional plasticizer molecules.[8] This was caused by an increase in the orientational mobility of the NLO molecules, due to the additional lowering of the T_g, resulting in a higher net alignment and hence a larger electrooptic effect. Moreover, in such compounds, the NLO molecules are reoriented under the influence of the space charge field. This leads to a spatial modulation of the birefringence and the electrooptic response, which greatly enhances the amplitude of the refractive index grating.[9] In this way, a number of polymeric composites with excellent performance, which approaches or even exceeds that of existing inorganic materials, have been reported.[8,10]

In this paper we report a systematic study of the effect of plasticization on the photorefractive performance of a particular PVK-based host−guest polymer. In this polymer, 0.1% of C_{60} is added to enhance the photogeneration process, while the electrooptic response is introduced by doping with 30% of the NLO molecule 4-(diethylamino)nitrobenzene (EPNA) (all percentages relative to the total film weight). As a plasticizer, *N*-ethylcarbazole (ECZ) was used, due to its similarity to the monomer unit of PVK. The paper is organized as follows: The effect of plasticization is described in section 3, followed by a more detailed study of the polymer composite that showed the best performance. This study includes the steady state photorefractive performance (section 4) and the kinetics of the grating growth (section 5). Finally, a new configuration is described in section 6, where prisms are employed to couple light into the sample.

2. Experimental Section

2.1. Sample Preparation. The compounds used for the preparation of the polymer composite were extensively purified before use. EPNA was synthesized by aromatic substitution of 4-fluoronitrobenzene with diethylamine and purified by

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double recrystallization from a dichloromethane/pentane (1:4) solution. PVK (secondary grade) was precipitated three times from chloroform in diethyl ether. ECZ was twice recrystallized from ethanol.

The electrooptic and photorefractive measurements were performed on approximately 100 μm thick polymer films. These films were prepared from chloroform solutions that contained proper amounts of the compounds. All the concentrations mentioned in the text are with respect to the total film weight. The solutions were filtered through a 0.2 μm filter, and the solvent was allowed to evaporate. Subsequently, the obtained solid film was reduced into powder and stored overnight in a vacuum chamber to ensure maximum solvent removal. The resulting powder was pressed in a stainless steel mold at elevated temperatures. After cooling, the resulting pellets were sandwiched between two indium tin oxide (ITO) covered glass plates by applying gentle pressure at 110 °C. The thickness was fixed by Teflon spacers. For the prism configuration, the samples were sandwiched between two prisms by means of Canadian balsam.

2.2. Measurements. The electrooptic coefficient of the samples was evaluated with the ellipsometric technique described by Schildkraut.[11] For the holographic studies of photorefractivity in polymers, the tilted geometry was used, with the two beams from a He−Ne laser incident on the sample at external angles 30° and 60°, unless otherwise stated. The grating spacing in this configuration was approximately 1.6 μm. The diffraction efficiency was measured in a backward degenerate four wave mixing (DFWM) arrangement. The grating was written using two *s*-polarized beams with the same power, equal to approximately 600 mW/cm^2 outside the sample, and the diffraction efficiency was measured using a weaker, p-polarized beam from a separate He−Ne laser. The phase shift of the photorefractive grating was measured with the two-beam coupling method,[12,13] using two p-polarized writing beams. For the evaluation of the gain coefficient (Γ), the energy exchange between two p-polarized beams, one of which was at least 10 times more intense, was measured. Γ was calculated from the equation[14]

$$\Gamma = (1/l)[\ln(\beta\gamma_0) - \ln(\beta+1-\gamma_0)] \quad (1)$$

where β is the ratio of the intensities of the pump and the probe before the sample, γ_0 is the ratio of the intensities of the probe beam, with and without the presence of the pump, and l is the propagation distance of the probe beam inside the sample. Experimental details can be found in ref 14.

3. Effect of Plasticization on the Photorefractive Performance of a Polymer

One of the most important parameters for photorefractive materials is the electrooptic coefficient, since, together with the amplitude of the space charge field, it determines the magnitude of the refractive index modulation. In polymers, the electrooptic coefficient depends on the concentration of NLO molecules, their molecular parameters such as hyperpolarizability and anisotropy, and their degree of alignment. In Figure 1 the temperature dependence of the electrooptic coefficient of the composite containing 30% EPNA and 0.1% C_{60} is depicted (squares). A considerable increase in electrooptic coefficient with temperature is observed. This increase is caused by the enhanced alignment of the NLO molecules, as the T_g is approached.

When 15% of PVK is replaced with ECZ, the temperature dependence of the electrooptic coefficient changes notably (Figure 1, circles). The electrooptic coefficient of the plasticized sample at room temperature is increased by a factor of 3 compared to that of the polymer without ECZ. However, these measurements were carried out at a modulation frequency of 1 kHz. In photorefractive materials, the electric field that causes the refractive index change (the space charge field) is a dc field. Therefore, the actual ratio between the electrooptic coefficient of the plasticized and the nonplasticized polymer may be different. The maximum electrooptic coefficient of the plasticized sample is reached around 50 °C, indicating that the flexibility of the polymer chains has increased but is not yet at its highest value.

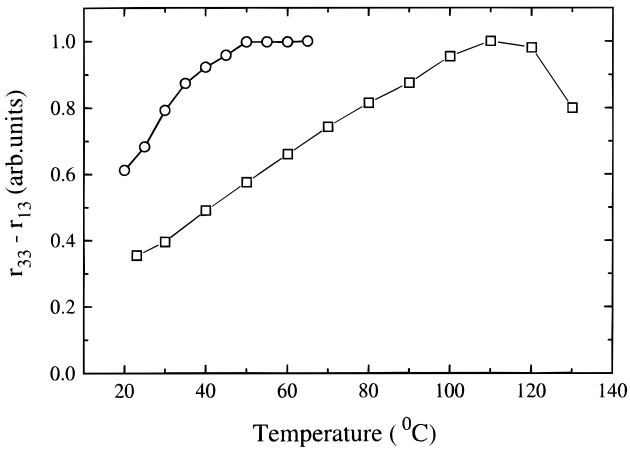

Figure 1. Electrooptic coefficient (measured at 1 kHz) of PVK(69.9%) C_{60}(0.1%) EPNA(30%) (squares) and PVK(54.9%) ECZ(15%) C_{60}-(0.1%) EPNA(30%) (circles) as a function of temperature.

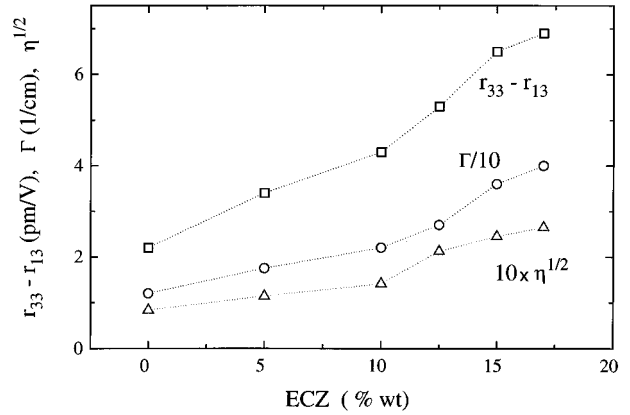

Figure 2. Variation of the electrooptic coefficient (at 20 V/μm and 1 kHz), the gain coefficient divided by 10 (at 55 V/μm), and the square root of the diffraction efficiency multiplied by 10 (at 55 V/μm) for the polymer PVK(69.9-*x*%) ECZ(*x*%) C_{60}(0.1%) EPNA(30%).

To systematically investigate the influence of plasticization on the magnitude of the refractive index modulation, the electrooptic coefficient, the diffraction efficiency (η), and gain coefficient (Γ) were measured for samples in which different amounts of PVK were substituted with ECZ. In Figure 2 the dependence of the electrooptic coefficient on ECZ concentration in the PVK composite is depicted (squares). A large increase in the electrooptic coefficient is observed with increasing ECZ concentration.

The material parameter that is directly influenced by the incorporation of additional plasticizer molecules is the T_g. To probe the dependence of the T_g on the ECZ concentrations. DSC measurements were performed on all the samples. However, due to the rather broad nature of the transition, it was not possible to obtain accurate values for the transition temperature. In Figure 3, two typical DSC traces are depicted: The upper one represents the heat flow for the sample containing 15% ECZ, while the lower one represents the heat flow for the unplasticized

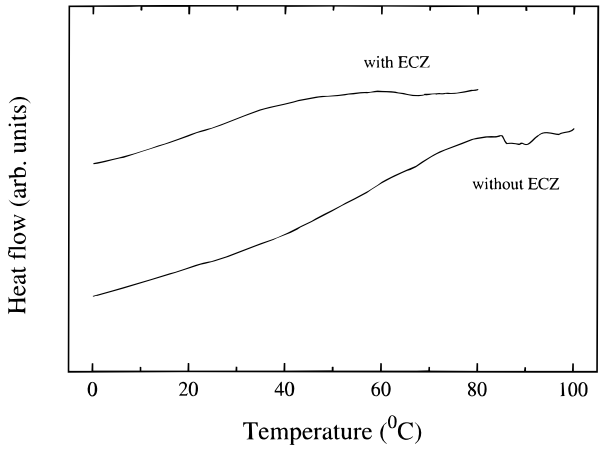

Figure 3. Heat flow of the polymers PVK(69.9%) C_{60}(0.1%) EPNA-(30%) (lower curve) and PVK(54.9%) ECZ(15%) C_{60}(0.1%) EPNA-(30%) (upper curve) as a function of the temperature as observed from a DSC experiment. The irregularity in the signal for the unplasticized sample that is observed immediately after the offset temperature is due to an experimental artifact.

sample. From this figure it is clear that the T_g of the polymer containing 15% ECZ has dropped considerably to lower temperatures compared to that of the unplasticized one.

Two important parameters that characterize the performance of photorefractive materials are the diffraction efficiency (η) and the gain coefficient (Γ), both of which are functions of the electrooptic coefficient:[15]

$$\eta \propto (r_{\text{eff}} E_{\text{sc}})^2 \tag{2}$$

$$\Gamma \propto r_{\text{eff}} E_{\text{sc}} \sin \varphi \tag{3}$$

where r_{eff} is the effective electrooptic coefficient, E_{sc} the space charge field, and φ the phase shift between the refractive index grating and the interference pattern. In Figure 2 the dependencies of the square root of the diffraction efficiency (triangles) and the gain coefficient (circles) on the ECZ concentration are depicted. Both quantities scale with the electrooptic coefficient, indicating that the space charge field formation is not affected by the addition of ECZ. This is also corroborated by the fact that, within experimental error, the response time for all the samples remained the same.

There is, however, an influence of the amount of ECZ on the stability of the sample with respect to crystallization. As PVK is substituted with ECZ and the amount of polymeric binder decreases, the tendency of the EPNA molecules to crystallize becomes apparent. The maximum concentration of ECZ investigated was 17.5%, since at higher concentrations the composites suffered from almost immediate crystallization of EPNA, making the material opaque and unsuitable for optical characterization. In samples with lower ECZ contents, crystallization was gradually evolving in time, depending on the total amount of dopants. For example, samples with 15% ECZ remained optically clear for more than a week, allowing a full characterization of the material. The crystallization of EPNA occurred only near the polymer−ITO interface and only in the section of the sample where an electric field was applied, indicating that the crystallization is electric field induced. The tendency of the NLO molecules to crystallize can be depressed by using a polymer with an intrinsically lower T_g, expelling the need for additional plasticization,[16] by using a liquid NLO molecule[17] or by using a NLO molecule that crystallizes much more difficultly.[18]

Another negative effect of plasticization is the lowering of the dielectric breakdown threshold of the samples. At ECZ concentrations higher than 15%, no electric fields above 60 V/μm could be applied without causing dielectrical breakdown of the sample. This was probably a result of the large ionic conductivity, due to the low T_g. Considering all the above observations, we selected the sample that contains 15% ECZ for further investigation.

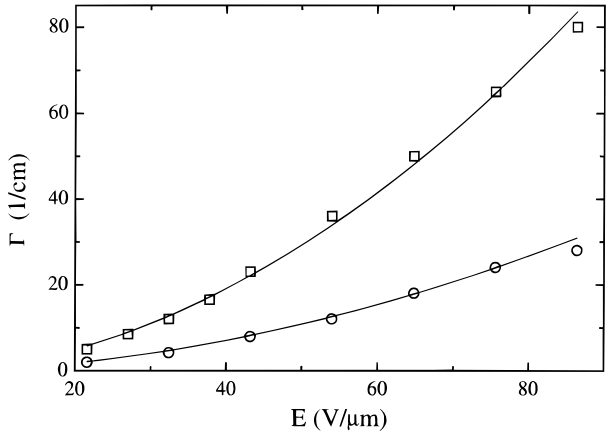

Figure 4. Electric field dependence of the gain coefficient of PVK-(54.9%) ECZ(15%) C_{60}(0.1%) EPNA(30%) (squares) and PVK(69.9%) C_{60}(0.1%) EPNA(30%) (circles). The curves are fits to a power law with exponents 1.9.

4. Steady State Properties of the Photorefractive Grating

The electric field dependencies of the gain coefficient of the plasticized and the unplasticized sample are depicted in Figure 4. The gain coefficient depends in a superlinear fashion on electric field. Such a dependence is typical for photorefractive polymers, as both the space charge field and the electrooptic coefficient are dependent on external electric field. Both the plasticized and the unplasticized polymer behave in approximately the same way, indicating again that plasticization does not affect the space charge field formation but only the magnitude of the electrooptic coefficient. The ratio between the two curves is 2.7, approximately equal to the ratio of their electrooptic coefficient. For the plasticized polymer a maximum value of 80 cm^{-1} at 85 V/μm was obtained.

The maximum value for the diffraction efficiency obtained in the plasticized sample was 20% at an external electric field of 85 V/μm. This value is approximately 8 times higher than observed for the nonplaticized composite. Larger values have been obtained for similar composites, using more efficient NLO molecules, at larger concentrations.[8,10]

Confirmation about the photorefractive nature of a refractive index grating can be obtained from the existence of a spatial phase shift between the illumination pattern and the refractive index grating. Investigation of the plasticized polymer composite revealed the existence of a refractive index grating that was approximately 25 $\pm$ 10° phase shifted with respect to the illumination pattern. Within experimental error, no electric field dependence of the phase shift was observed in the range 40−85 V/μm.

The question arises whether the measured phase shift is an intrinsic property of the photorefractive grating or if it is caused by the coexistence of a local grating. To check that, a two-beam coupling experiment was performed in the early stage of grating growth. In the case of coexistence of two gratings, one would expect the value of the phase shift to change in time. The experiment however yielded the same value as that in steady state conditions, which indicates that in PVK/ECZ/C_{60}/EPNA only one grating is produced by illumination, the photorefractive one.

The low value of the phase shift suggests a large value for the saturation field, which implies a high trap density. Ac-

cording to the standard model of photorefractivity, the phase shift is given by (in the case where the diffusion field is ignored)[19]

$$\varphi = \arctan(E_K/E_S) \quad (4)$$

where E_K is the projection of the applied electric field on the grating wave vector and E_S is the saturation field. According to eq 4, the phase shift for $E_K < E_S$ is between 0° and 90°, while at high fields ($E_K \gg E_S$) the phase shift approaches 90°. Even though this equation was derived for inorganic crystals, it has been shown to qualitatively describe the behavior of the phase shift in polymeric photorefractive materials at sufficiently high electric fields.[4] The saturation field is given by[15]

$$E_S = eN_{PR}/\epsilon\epsilon_0 K_G \quad (5)$$

where N_{PR} is the effective trap density, ϵ the dielectric constant relative to the permittivity of free space, ϵ_0, and K_G the grating wave vector. The observed value of the phase shift corresponds to a trap density on the order of 5×10^{16} cm^{-3}. Similar values have been estimated in other photorefractive polymers.[4,20]

An indication of a large saturation field has already been obtained from the superlinear dependence of the gain coefficient with an external electric field (Figure 4). Such a superlinear dependence can only occur if both the electrooptic coefficient and the space charge field increase with increasing external electric field (eq 3). The space charge field, in the case where the diffusion field is ignored, is given by[15]

$$E_{sc} = mE_K[1 + (E_K/E_S)^2]^{-0.5} \quad (6)$$

where m is the modulation of the illumination pattern. According to the above, the superlinear increase of the gain coefficient indicates that the saturation field in PVK/ECZ/C_{60}/EPNA is larger than or comparable to the applied field.

The saturation field can be decreased by increasing the grating wave vector, i.e., lowering the spacing between the interference fringes (eq 5). However, K_G cannot be increased dramatically in the usual tilted geometry. For this reason another configuration was used to write the photorefractive grating, in which the two writing beams are incident on the sample from opposite sides (reflection geometry) at an angle of 45° with the sample normal. In this way an interference pattern is created with a grating spacing of 0.2 μm, resulting in a smaller saturation field and additionally a larger projection of the external electric field onto the interference pattern. The phase shift of the photorefractive grating was found to be approximately 80 ± 10°. This result further corroborates the conclusion that the low phase shift observed in the tilted geometry is a genuine property of the photorefractive grating that can be attributed to a large density of trapping sites.

5. Kinetics of the Photorefractive Grating

The kinetics of the formation and erasure of the photorefractive grating was investigated using degenerate four-wave mixing. In the inset of Figure 5, a typical write−erase cycle is shown. The arrows mark the position at which the second writing beam was turned on and subsequently turned off. Quantitative information about the grating growth can be obtained using the single-carrier model of photorefractivity in the limit where the decay of the diffraction efficiency is related to the space charge field decay. In this case, the diffraction efficiency obeys the law[15]

$$\eta(t) = \eta(0) \exp[-2t/\tau] \quad (7)$$

where τ is the characteristic response time and $\eta(0)$ the steady state diffraction efficiency. For the space charge field formation, charges have to be generated and transported to the dark regions. Consequently, the response time is determined by the illumination intensity, the efficiency of charge generation, and their drift mobility. In PVK/ECZ/C_{60}/EPNA, the response time is typically on the order of 1 s. However, according to holographic time-of-flight measurements, charge carriers in PVK can move distances on the order of the grating spacing within several milliseconds,[21] indicating that charge transport is not the limiting factor.

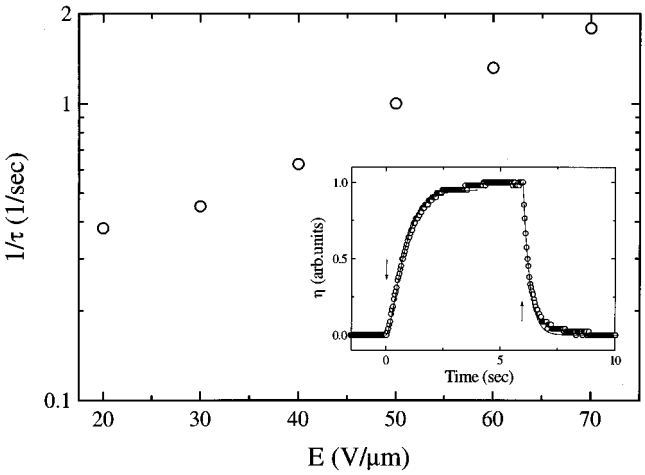

Figure 5. Electric field dependence of the response speed of PVK-(54.9%) ECZ(15%) C_{60}(0.1%) EPNA(30%) under uniform illumination of 500 mW/cm^2. The inset shows the time dependence of the diffraction efficiency as obtained from degenerate four-wave mixing. The line is a fit to eq 7, yielding a response time of 0.6 ± 0.1 s.

In Figure 5, the dependence of the response speed on the applied field is shown. The data are reminiscent of a dependence of the quantum yield of charge generation (ϕ) as predicted by the Onsager theory of geminate recombination.[22] According to this theory, ϕ, which levels off at low electric fields, follows a power law-like dependence at higher electric fields, with a slope that depends on the initial electron−hole separation. Thus, the response time of PVK/ECZ/C_{60}/EPNA seems to be limited by photogeneration. The same conclusion has been reached for other photorefractive polymers.[17,23]

From the single-carrier model of photorefractivity the response speed is expected to be a linear function of the erasing beam intensity. We have investigated the dependence of the response speed on erasing beam intensity and found a sublinear power law dependence with an exponent of 0.65 ± 0.05. This deviation from the single-carrier model has been observed in other photorefractive polymers, and it is attributed to a high density of shallow trapping sites.[10]

The dark decay of the diffraction efficiency was measured while applying an electric field of 55 V/μm. The diffraction efficiency decays with two time scales: a first, rapid decay to approximately 75% of its initial value, followed by a second, slower decay. The initial component is presumably caused by the emptying of the shallow traps, whose existence was already indicated from the sublinear dependence of the response time with light intensity. The slow decay was fitted to an exponential function: $\eta \propto \exp[-2t/\tau_{dark}]$. From this fit a dark storage time (τ_{dark}) of approximately 16 min was calculated. The reason for such a short decay time is not known, because no detailed investigation was carried out.

6. Prism Configuration

Most photorefractive polymers reported so far have been characterized in the tilted geometry, in which the two writing beams approach the sample from the same direction. This is

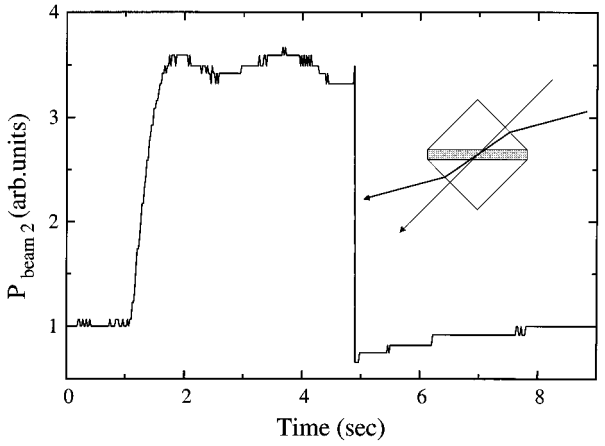

Figure 6. Time dependence of the transmitted power of the probe beam as observed in a two-beam coupling experiment in the prism configuration in PVK(54.9%) ECZ(15%) C_{60}(0.1%) EPNA(30%), at 85 V/μm. The inset shows a schematical representation of the prism configuration.

not the best geometry for an optimized photorefractive response since it does not allow a large projection of grating wave vector along the applied electric field. There are several ways to increase this projection. One way is by utilizing the previously described reflection geometry, where the grating wave vector is parallel to the applied electric field, creating the largest possible projection. The drawback of this geometry is the decrease in the grating spacing, which results in a smaller saturation field and hence in a decrease in the magnitude of the refractive index modulation. There is however another geometry in which the projection of the applied electric field can be somewhat improved. In this geometry, two prisms are used to couple the laser beams to and from the sample. The two writing beams are incident on the sample from the same direction, creating an interference pattern with approximately the same grating spacing and hence the same saturation field as in the usual tilted geometry. By means of the prism the angle between the grating wave vector and the applied electric field is decreased, resulting in a larger projection of the grating wave vector along the applied field. Furthermore, two additional effects occur: First the propagation length of the beams inside the sample is increased, which allows a larger interaction between the laser beams to take place. Second, due to a larger contribution from r_{33}, the effective electrooptic coefficient increases.[9]

In Figure 6 the transmitted power of the weak writing beam is probed in the two-beam coupling experiment using the prism geometry at an applied electric field of 85 V/μm. At $t \approx 1$ s the pump beam is turned on, causing energy to flow from beam 2 to beam 1 as the photorefractive grating is created. The energy exchange reaches a constant level, at which the probe beam is approximately 3 times amplified. Then at $t \approx 5$ s the pump beam is turned off, causing a decay in the transmitted energy of beam 1 due to its diffraction by the photorefractive grating, which gradually comes back to its initial value as the photorefractive grating is erased. Using two writing beams with approximately equal intensity, a diffraction efficiency in excess of 70% at 85 V/μm was measured. Compared with the values observed in the tilted geometry without prism couplers, the gain per pass has almost doubled its value and the diffraction efficiency has increased 4 times.

7. Conclusions

The performance of poly(*N*-vinylcarbazole) (PVK) based photorefractive polymers can be greatly enhanced by sufficient plastification. In PVK this can effectively be done by incorporating large amounts of *N*-ethylcarbazole (ECZ). The observed increase in photorefractive performance was solely due to an increased electrooptic effect and was not caused by the alteration of the space charge field. Incorporation of large amounts of ECZ, however, did lead to a lower stability of the sample toward the electric field. And more importantly the tendency of the EPNA molecules to phase-separate is greatly enhanced.

The steady state photorefractive response in PVK-based polymers suggests a high value of the saturation field, while the kinetics of the grating growth and erasure are dominated by photogeneration.

An additional improvement of the photorefractive performance can be achieved by increasing the projection of the external electric field onto the interference pattern, while keeping the same grating spacing, by means of a simple light-coupling system. Using two prisms to couple the light in and out of the sample, a large increase in the gain coefficient and the diffraction efficiency was observed.

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